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(54) **Porous film.**

(57) Disclosed is a breathable, hydrolyzable, porous film which is obtained by the process comprising adding from 40 to 250 parts by weight of a finely-powdered filler having an average particle size of from 0.3 to 4 μ m to 100 parts by weight of a polylactic acid-base resin composition comprising from 80 to 100 % by weight of polylactic acid or a lactic acid-hydroxycarboxylic acid copolymer and from 0 to 20 % by weight of a plasticizer, melting and film-forming the resultant mixture, and successively stretching the thus-obtained film 1.1 times or more to at least one direction of the axis; and which is consequently useful as a material for leakproof films of sanitary materials such as a paper diaper and packaging materials, and does not accumulate as wastes because of hydrolyzability in the natural environment in the case of being abandoned after use.

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The present invention relates to a porous film, and particularly relates to a hydrolyzable, porous film which comprises a polylactic acid-base resin composition essentially consisting of a lactic acid-base polymer having hydrolyzability in the natural environment and a finely-powdered filler.

The porous film of the invention has high moisture permeability and breathability and is also excellent in flexibility, and is hence suitable for uses such as leak-proof films for a disposable paper diaper and other sanitary materials, packaging materials and filter media. Additionally the porous film is prepared from the polylactic acid-base resin composition and has hydrolyzability. Consequently, the porous, film is expected for a counter-measure of waste disposal which has recently been a serious problem.

Porous films have already been prepared by blending a specific proportion of an organic or inorganic incompatible matter with polyolefin-base resin, melting, film-forming and stretching the resultant film as disclosed in Japanese Patent Publication Sho 53-12542 and Japanese Laid-Open Patent Sho 56-99242, 57-59727, 60-129240 and 62-138541.

These porous films are mainly used for leakproof films for sanitary materials such as a disposable paper diaper and packaging materials, and are generally applied to so-called throw away uses where the films are abandoned immediately after use.

However, the porous films prepared from polyolefin-base resin cannot be hydrolyzed or have a very slow rate of hydrolysis in the natural environment. As a result, these film remain semipermanently when buried under the ground after use. Disposal of these films in the ocean causes damage of a view or destruction of the living environment of marine organisms. Thus, disposal of wastes has become a social problem with expansion of consumption.

On the other hand, polylactic acid and its copolymer have been known as a thermoplastic and hydrolyzable polymer. For example, USP 1,995,970 discloses a preparation process of a lactic acid-base polymer by polymerization of lactic acid, lactide or a mixture of these compounds.

These lactic acid-base polymers can be obtained by fermentation of inexpensive materials such as corn starch and corn syrup and can also be prepared from petrochemicals such as ethylene. The lactic acid-base polymer, however, is generally high in hardness and hence has a disadvantage of lacking in flexibility when used in the form of a film. Consequently, the lactic acid-base polymer has been thought to have many restrictions in use and a porous film of the lactic acid-base polymer has not yet been known.

That is, a porous film consisting of polylactic acid or its copolymer which has hydrolyzability in the natural environment has not yet been known and is a material for providing useful goods in view of the above market demand and protection of the natural environment. Thus, the development of the lactic acid-base porous films has been strongly desired.

Embodiments of the present invention desirably provide a porous film which is plasticized, if desired, and has hydrolyzability.

As a result of an intensive investigation the present inventors have found that a porous film having suitable flexibility and hydrolyzability can be obtained by adding a specific amount of a finely-powdered filler to a specific amount of a polylactic acid-base resin composition comprising a specific amount of a lactic acid-base polymer and a specific amount of a plasticizer, melting and film-forming the resultant mixture, and stretching the thus-obtained film. Thus, the present invention has been completed.

An aspect of the present invention is a porous film obtained by the process comprising adding from 40 to 250 parts by weight of a finely-powdered filler having an average particle size of from 0.3 to 4 μ m to 100 parts by weight of a polylactic acid-base resin composition comprising from 80 to 100 % by weight of polylactic acid or a lactic acid-hydroxycarboxylic acid copolymer and from 0 to 20 % by weight of a plasticizer, melting and film-forming the resultant mixture, and successively stretching the thus-obtained film 1.1 times or more to at least one direction of the axis.

The hydrolyzable, porous film of the invention is characterized in hydrolyzability and may be prepared by adding the finely-powdered filler having a specific particle size to the polylactic acid-base resin composition having a specific composition, mixing for example with a Henschel mixer, successively melt-kneading after pelletizing or as intact with a single- or twin-screw extruder, delivering through a ring or flat die to form a film, and stretching to provide porosity for the thus-obtained film.

The porous film of the invention has breathability, can provide various grades of flexibility and stiffness, and additionally is hydrolyzable. Consequently, the film is useful as a material for leakproof films of sanitary materials such as a paper diaper and packaging materials. The film is hydrolyzed in the natural environment in the case of discarding after use and hence does not accumulate in the form of industrial wastes.

The lactic acid-base polymer of the present invention is polylactic acid or a copolymer of lactic acid and hydroxycarboxylic acid. Exemplary hydroxycarboxylic acid includes glycolic acid, hydroxybutyric acid, hydroxyvaleric acid, hydroxypentanoic acid, hydroxycaproic acid and hydroxyheptanoic acid. Preferred hydroxycarboxylic acid is glycolic acid and hydroxycaproic acid.

Preferred molecular structure of polylactic acid is composed of from 85 to 100 % by mole of an L-lactic acid unit or D-lactic acid unit and from 0 to 15 % by mole of the antipode unit of each lactic acid. The copolymer of lactic acid and hydroxycarboxylic acid is composed of from 85 to less than 100 % by mole of an L-lactic acid unit or D-lactic acid unit and less than 15 % by mole of a hydroxycarboxylic acid unit.

The lactic acid-base polymer can be prepared by selecting the raw material monomer required for obtaining a desired polymer structure from L-lactic acid, D-lactic acid and hydroxycarboxylic acid and carrying out dehydrating polycondensation. The polymer can be preferably prepared by using lactide which is a cyclic dimer of lactic acid, glycolide which is a cyclic dimer of glycolic acid, and caprolactone and carrying out ring-opening polymerization.

The lactide includes L-lactide which is a cyclic dimer of L-lactic acid, D-lactide which is a cyclic dimer of D-lactic acid, meso-lactide obtained by cyclizing dimerization of D-lactic acid and L-lactic acid, and DL-lactide which is a racemic mixture of D-lactide and L-lactide. Any of these compounds can be used for the invention.

However, preferred main materials are D-lactide and L-lactide.

The lactic acid-base polymer which can be preferably, used for the invention is a lactic acid-base polymer essentially consisting of from 85 to 100 % by mole of an L-lactic acid unit or D-lactic acid unit and from 0 to 15 % by mole of the antipode lactic acid unit and/or glycolic acid unit.

The lactic acid-base polymer can be prepared by the following processes ① to ⑥.

① About 85 % by mole or more of L-lactide is copolymerized with about 15 % by mole or less of D-lactide and/or glycolide.

② About 85 % by mole or more of D-lactide is copolymerized with about 15 % by mole or less of L-lactide and/or glycolide.

③ About 70 % by mole or more of L-lactide is copolymerized with about 30 % by mole or less of DL-lactide and/or glycolide.

④ About 70 % by mole or more of L-lactide is copolymerized with about 30 % by mole or less of meso-lactide and/or glycolide.

⑤ About 70 % by mole or more of D-lactide is copolymerized with about 30 % by mole or less of DL-lactide and/or glycolide.

⑥ About 70 % by mole or more of D-lactide is copolymerized with about 30 % by mole or less of meso-lactide and/or glycolide.

The lactic acid-base polymer has preferably a high molecular weight. The inherent viscosity of the polymer at 25 °C in a chloroform solution having a concentration of 0.5 g/dl is preferably 1 ~ 10, more preferably 3 ~ 7.

When the inherent viscosity is less than 1, melt viscosity is too low, the polymer causes drooling from the die slit of the extruder and thus processing becomes difficult. Additionally, the product thus obtained is very brittle and difficult to handle. On the other hand, the inherent viscosity exceeding 10 causes too high melt viscosity and unfavorably gives adverse effect on the melt extrudability of the polymer.

Catalysts are preferably used in order to obtain a high molecular weight polymer within a short time by the polymerization of lactide or copolymerization of lactide and glycolide.

The polymerization catalysts which can be used are various compounds capable of exhibiting catalytic effect on the polymerization reaction. Exemplary catalysts include stannous octoate, tin tetrachloride, zinc chloride, titanium tetrachloride, iron chloride, boron trifluoride ether complex, aluminum chloride, antimony trifluoride, lead oxide and other polyvalent metal compounds. Tin compounds and zinc compounds are preferably used. Stannous octoate is particularly preferred in these tin compounds. The amount is preferably in the range of from 0.001 to 0.1 % by weight for the weight of lactide or the total weight of lactide and glycolide.

Known chain extenders can be used for the polymerization. Preferred chain extenders are higher alcohols such as lauryl alcohol and hydroxy acids such as lactic acid and glycolic acid. Polymerization rate increases in the presence of a chain extender and polymer can be obtained within a short time. Molecular weight of the polymer can also be controlled by varying the amount of the chain extender. However, too much amount of the chain extender tends to decrease molecular weight of polymer formed. Hence, the amount of the chain extender is preferably 0.1 % by weight or less for lactide or for the total weight of lactide and glycolide.

Polymerization or copolymerization can be carried out in the presence or absence of a solvent. Bulk polymerization in a molten state of lactide or glycolide is preferably carried out in order to obtain high molecular weight polymer.

In the case of molten polymerization, polymerization temperature may be generally above the melting point (around 90 °C) of the monomer, lactide or glycolide. In the case of solution polymerization which uses solvents such as chloroform, polymerization can be carried out at temperature below the melting point of lactide or glycolide. In any case, polymerization temperature above 250 °C is unfavorable because decomposition of formed polymer develops.

The polylactic acid-base resin composition of the invention comprises from 80 to 100 % by weight of the above lactic acid-base polymer and from 0 to 20 % by weight of a plasticizer.

The plasticizers which can be used include, for example, di-n-octyl phthalate, di-2-ethylhexyl phthalate, dibenzyl phthalate, di-iso-octyl phthalate and other phthalic acid derivatives; di-n-butyl adipate, dioctyl adipate and other adipic acid derivatives; di-n-butyl maleate and other maleic acid derivatives; tri-n-butyl citrate and other citric acid derivatives; monobutyl itaconate and other itaconic acid derivatives; butyl oleate and other oleic acid derivatives; glycerol monoricinolate and other ricinoleic acid derivatives; tricresyl phosphate, trixylenyl phosphate and other phosphoric acid esters; lactic acid, straight chain lactic acid oligomer, cyclic lactic acid oligomer and lactide. These plasticizers can be used singly or as a mixture. In these plasticizers, lactic acid, straight chain lactic acid oligomer, cyclic lactic acid oligomer and lactide are preferably used in view of plasticizing effect. Lactic acid oligomers used for the plasticizer can be prepared with ease by hot-dehydrating condensation of lactic acid at 50 to 280°C.

The oligomer thus obtained usually has a polymerization degree in the range of from 1 to 30. The oligomer can also be prepared by heating glycolide or lactide at 50 to 280 °C in the presence of water and glycolic acid or lactic acid. The oligomer also includes lactide, i.e., cyclic dimer of lactic acid which is used as a monomer in the preparation of lactic acid-base polymer.

The lactic acid-base polymer is effectively plasticized by the addition of the plasticizer and resulting resin composition becomes flexible. When the amount of the plasticizer is 5 % by weight or more, flexibility can be clearly observed. However, the amount exceeding 20 % by weight gives adverse effect on the melt-extension and stretching of the resin composition and unfavorably decreases mechanical strength of the porous film obtained.

The plasticizer is blended with the lactic acid-base polymer by dissolving the polymer in a solvent such as chloroform, methylene chloride, toluene or xylene, or heat-melting the polymer at 100 to 280 °C, and thereafter adding and mixing a prescribed amount of the plasticizer.

Lactic acid or lactic acid oligomer including lactide which is a preferred plasticizer is mixed, for example, by the following methods:

- (a) Polymerization of lactide or copolymerization of lactide and glycolide is stopped before completion to leave unreacted lactide.
- (b) After completing polymerization of lactide or copolymerization of lactide and glycolide, a prescribed amount of lactic acid or a lactic acid oligomer including lactide is added and mixed. Methods (a) and (b) can be incorporated.

In the method (a), unreacted lactide is uniformly mixed with the lactic acid-base polymer on microscopic observations and exhibits good plasticizing performance. Reaction of monomer (lactide) is started by heating in the presence of a catalyst, in the coexistence of a chain extender, if desired, and stopped by finishing the heating at the time when the residual monomer concentration is reached to a prescribed level. The amount of residual monomer in the resulting lactic acid-base polymer can be determined by gas chromatographic analysis or thermogravimetric analysis.

In the method (b), after finishing polymerization, resulting lactic acid-base polymer is dissolved in a solvent such as chloroform, methylene chloride, toluene and xylene, or heat-melted at temperature of 100 to 280 °C and successively a prescribed amount of lactic acid or the lactic acid oligomer is added and mixed. The method has an advantage of readily controlling the amount of lactic acid or the lactic acid oligomer in the resin composition.

The polylactic acid-base resin composition obtained above is compression-molded or melt-extruded at temperature of 180 to 280 °C into films, sheets or bars. These molded articles are cooled to about -20 °C with dry ice-methanol and crushed with a hammer mill. Alternatively, the resin composition can also be melt-extruded into a strand and cut into pellets.

The polylactic acid-base resin composition thus crushed or pelletized is then mixed with a finely-powdered filler.

The finelypowdered filler may be mixed with the lactic acid-base polymer simultaneously with blending of the plasticizer.

The finely-powdered filler which can be used for the invention is inorganic or organic fine powder.

Exemplary inorganic fine powder includes calcium carbonate, magnesium carbonate, barium carbonate, magnesium sulfate, barium sulfate, calcium sulfate, zinc oxide, magnesium oxide, calcium oxide, titanium oxide, barium oxide, aluminium oxide, aluminium hydroxide, hydroxyapatite, silica, mica, talc, kaolin, clay, glass powder, asbestos powder, zeolite and acid clay. Particularly preferred inorganic fillers are calcium carbonate, magnesium oxide, barium sulfate, silica and acid clay.

The organic fine powder includes, for example, wood flour, pulp powder and other cellulosic powder.

The finely-powdered filler preferably has an average particle size of from 0.3 to 4 µm, and more preferably

has a specific surface area of 15 m²/g or less in addition to this range of the average particle size. The most preferred filler has a specific surface area in the range of from 0.5 to 5 m²/g.

The average particle size exceeding 4 μm gives adverse effect on the stretching ability of the film and sometimes leads to film breakage prior to uniform whitening. Consequently, stability of operation becomes poor and uniform porosity of the film is difficult to obtain. When the average particle size is less than 0.3 μm, high filling of the inorganic fine particle becomes difficult and it is impossible to make the film porous. On the other hand, when the specific surface area exceeds 15 mm²/g, the form of the inorganic finely-powdered filler becomes amorphous, needle or plate. Consequently, particle size distribution becomes broad, stretching ability of the film decreases, and processing ability for making the porous film is unfavorably impaired.

The amount of the finely-powdered filler for use in the invention is from 40 to 250 parts by weight, preferably from 60 to 150 parts by weight per 100 parts by weight of the polylactic acid-base resin composition. The amount less than 40 parts by weight leads to insufficient porosity and low percentage of open cells, and hence satisfactory breathability and moisture permeability cannot be obtained. On the other hand, the amount exceeding 250 parts by weight gives adverse effect on the melt-extendability, film-forming ability and stretching ability.

Next, an example of the preparation process of the porous film of the invention will be illustrated.

The finely-powdered filler is added to the polylactic acid-base resin composition, mixed for 5 to 30 minutes at room temperature with a blender such as Henschel mixer, super mixer and tumbling mixer, followed by melt-kneading with a common single- or twin-screw extruder and pelletizing the extrudate.

The pellets thus-obtained are successively processed into a film by an inflation method or T-die extrusion method. The film can also be obtained directly from the extruder without pelletizing.

Extrusion temperature is preferably in the range of from 100 to 270 °C, more preferably in the range of from 130 to 250 °C. When the temperature is lower than 100 °C, extrusion stability is difficult to obtain and overload is liable to occur. On the other hand, the temperature exceeding 270 °C is unfavorable because decomposition of the lactic acid-base polymer becomes violent.

The die of the extruder used in the invention is a ring or flat die. Temperature range of the die is about the same as extruding temperature.

Successively, the extrudate is stretched from 1.1 to 10 times, preferably from 1.1 to 7 times at least to one direction of axis. Stretching can be carried out in multi-steps or conducted biaxially. When the degree of stretching is less than 1.1 times, the porosity of the film is unsatisfactory. The degree of stretching exceeding 10 times often leads to unfavorable breakage of the film.

Preferred stretching temperature is in the range of from the glass transition temperature (T_g) of the lactic acid-base polymer to T_g + 50 °C. After stretching, heat setting can be carried out in order to enhance form stability of the pore.

Thickness of the porous film differs depending upon uses and is generally in the range of from 10 to 300 μm.

Colorants, reinforcements and other types of fillers can also be added unless the object of the invention is impaired.

The present invention will hereinafter be illustrated further in detail by way of examples.

Following evaluation methods were used in the examples.

① Amount of residual monomer

After finishing the polymerization reaction, the reaction mixture was dissolved in hexafluoroisopropanol (hereinafter referred to as HFIP) or methylene chloride to obtain a solution having known concentration. Residual monomer was determined by gas chromatography.

② Inherent viscosity

A lactic acid-base polymer is dissolved in chloroform (concentration ; 0.5 g/dl), viscosity of the resulting solution was measured at 25 ± 0.5 °C with a Ubbelohde viscometer, and inherent viscosity η was calculated from the following equation.

$$\eta = \log(T_1/T_0)/C$$

wherein

T₀ : Measuring time of the solvent (sec)

T₁ : Measuring time of the solution (sec)

C : concentration of the sample solution (g/dl)

③ Specific surface area

Measured by the BET absorption method

5 ④ Average particle size

A powder specific surface area tester (permeation method) Model SS-100 (manufactured by Shimadzu Seisaku-sho co.) was used. To a sample cylinder having a sectional area of 2 cm² and a height of 1 cm, 3 g of the sample was filled, and the average particle size was calculated from the time required for permeating 50 cc of the air through the filled layer under the pressure of 500 mmH₂O.

⑤ Permeability

Measured in accordance with ASTM-E-96-66

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⑥ Polymerization degree of oligomer

An oligomer was dissolved in tetrahydrofuran or chloroform, distribution of the polymerization degree was measured by gel permeation chromatography (GPC) to calculate polymerization degree of the oligomer.

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Preparation Example

To a reaction vessel, 1.8 kg of L-lactide and 1.0 kg of an aqueous lactic acid solution having a concentration of 87 % by weight were charged and heated for 2 hours at 100 °C. The reaction mixture was cooled to the room temperature. A viscous transparent liquid was obtained. As a result of GPC analysis, the liquid contained lactic acid and a lactic acid oligomer. An average polymerization degree was 2.8. The product was hereinafter referred to as LA-oligomer.

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Examples 1 ~ 15, and Comparative Examples 1 ~ 3

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Marketed L-lactide (hereinafter referred to as L-LTD), D-lactide (hereinafter referred to as D-LTD), DL-lactide (hereinafter referred to as DL-LTD) and glycolide (hereinafter referred to as GLD) were individually recrystallized 4 times from ethyl acetate.

ε -Caprolactone (hereinafter referred to as CL) was dried over calcium hydride and distilled.

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To a glass reaction vessel having a silane-treated internal surface, the above-purified L-LTD, D-LTD, DL-LTD, GLD, CL and a catalyst stannous octoate were respectively charged in an amount illustrated in Table 1. Then the resulting mixture was dried for 24 hours by evacuating the reaction vessel.

The reaction vessel was heated to the prescribed temperature illustrated in Table 1 and polymerization was carried out for the prescribed time. After finishing the reaction, the reaction mixture was discharged from the vessel. The lactic acid-base polymers thus-obtained were referred to as P1 ~ P6.

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The inherent viscosity and residual monomer content were measured and results are illustrated in Table 1.

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Table 1

5	Lactic acid-base polymer	P1	P2	P3	P4	P5	P6
	L-LTD (wt. parts)	100	70	95	75	50	80
10	DL-LTD(wt. parts)	—	30	—	30	50	—
	D-LTD (wt. parts)	—	—	5	—	—	—
	GLD (wt. parts)	—	—	—	5	—	
15	CL (wt. parts)	—	—	—	—	—	20
	Catalyst (wt. %)	0.015	0.015	0.015	0.015	0.015	0.015
20	Polymerization temperature(°C)	110	120	110	120	125	120
	Polymerization time (hr)	160	120	40	120	100	140
25	Inherent viscosity	4.2	6.1	3.8	5.1	5.4	4.3
30	Residual monomer (wt. %)	1.3	0.9	13.1	1.1	1.5	1.9

Next, L-LTD or LA-oligomer obtained in Preparation Example was added to these lactic acid-base polymers in a proportion illustrated in Table 2, mixed with a plastomill at temperature illustrated in Table 2 to obtain poly-lactic acid-base resin compositions C1 to C7.

These resin compositions were pressed under the pressure of 100 kg/cm² at the temperature illustrated in Table 2 to obtain a sheet having a thickness of 1 mm.

Table 2

Composition	C1	C2	C3	C4	C5	C6	C7
Lactic acid-base polymer (wt. %)	P1	P2	P2	P2	P4	P5	P6
	80	90	80	90	80	90	90
Additive (wt. %)	LA oligo-mer	LA oligo-mer	LA oligo-mer	LTD mono-mer	LA oligo-mer	LA oligo-mer	LA oligo-mer
	20	10	20	10	20	10	10
Melt-mixing temperature (°C)	210	150	150	150	150	130	130
Press temperature (°C)	210	150	150	150	150	130	130

The polylactic acid-base resin composition illustrated in Table 3 was cooled with liquid nitrogen, crushed with a hammer mill, and followed by adding a finely-powdered filler having an average particle size illustrated in Table 3 in an amount illustrated in Table 3 for 100 parts by weight of the polylactic acid-base resin composition and mixing with a Henschel mixer at the room temperature. The resulting mixture was pelletized with a twin-screw extruder. The pellets obtained were melted with a single-screw extruder and delivered through a T-die at 230°C. The extruded film was formed so as to give, after stretching, a porous film having a thickness illustrated in Table 4.

Successively, the film was stretched with rolls at 60°C to the uniaxial or biaxial direction with a degree of stretching illustrated in Table 4 to obtain a porous film.

Properties of the porous film thus-obtained were evaluated and results are illustrated in Table 4.

Next, the porous film obtained in Examples 1,2 and 5 and a porous film of polyolefin resin (Espol N; Trade Mark of Mitsui Toatsu Chemicals Inc.) were respectively immersed in distilled water at 37 °C . After 120 days, weight loss was 7 %, 13 %, 21 % and 0 %, respectively.

Table 3

	Polylactic acid-base resin composition	Finely-powdered filler		
		Compound	Average particle size (μ m)	Amount (wt part)
<u>Example</u>				
1	P1	Precipitated BaSO ₄	0.8	200
2	P2	↑	0.8	120
3	P3	↑	0.5	50
4	P5	MgO	1.1	80
5	P6	Precipitated BaSO ₄	1.1	120
6	C1	↑	1.1	120
7	C2	↑	1.1	120
8	C2	Precipitated CaCO ₃	0.8	120
9	C2	↑	0.5	80
10	C3	↑	0.5	50
11	C4	Heavy CaCO ₃	2.6	120
12	C5	Precipitated BaSO ₄	3.0	120
13	C5	↑	3.5	120
14	C7	↑	3.5	120
<u>Comparative Example</u>				
1	P1	—	—	0
2	P1	Precipitated BaSO ₄	0.8	30
3	C2	↑	0.8	300

Table 4

	Degree of stretching (times)	Thickness (μm)	Permeability ($\text{g/m}^2 / 24\text{hr}$)	Remark
<u>Example</u>				
1	2	36	1500	
2	7	35	2500	
3	3 \times 3	35	5500	
4	5	34	1800	
5	4	36	2100	
6	7	36	2400	
7	5	35	2200	
8	5	36	2100	
9	5	34	1900	
10	5	35	1700	
11	5	36	2400	
12	5	35	2500	
13	5	35	2800	
14	5	35	2500	
<u>Comparative Example</u>				
1	1	34	220	unstretched
2	7	36	less than 400	fluctuated permeability
3	—	—	—	extrusion impossible

Claims

1. A porous film as obtainable by the process comprising adding from 40 to 250 parts by weight of a finely-powdered filler having an average particle size of from 0.3 to 4 μm to 100 parts by weight of a polylactic acid-base resin composition comprising from 80 to 100 % by weight of polylactic acid or a lactic acid-hydroxycarboxylic acid copolymer and from 0 to 20 % by weight of a plasticizer, melting and film-forming the resultant mixture, and successively stretching the thus-obtained film 1.1 times or more to at least one direction of the axis.
2. The porous film of claim 1 wherein polylactic acid comprises from 85 to 100 % by mole of an L-lactic acid unit and from 0 to 15 % by mole of a D-lactic acid unit, or from 85 to 100 % by mole a D-lactic acid unit and from 0 to 15 % by mole of an L-lactic acid unit.
3. The porous film of claim 1 wherein the lactic acid-hydroxycarboxylic acid copolymer comprises from 85 to 100 % by mole of an L-lactic acid unit and from 0 to 15 % by mole of a glycolic acid unit, or from 85 to 100 % by mole of a D-lactic acid unit and from 0 to 15 % by mole of a glycolic acid unit.
4. The porous film of any one of the preceding claims wherein the plasticizer is lactic acid, a lactic acid oligomer or lactide.
5. The porous film of any one of the preceding claims wherein the finely-powdered filler is inorganic powder.
6. A porous film of claim 1 wherein polylactic acid (A) comprises from 85 to 100 % by mole of an L-lactic acid

unit and from 0 to 15 % by mole of a D-lactic acid unit, the lactic acid-hydroxycarboxylic acid copolymer (B) comprises from 85 to 100 % by mole of an L-lactic unit or from 85 to 100 % by mole of a D-lactic acid unit and from 0 to 15 % by mole of a glycolic acid unit, the plasticizer (C) is lactic acid, a lactic acid oligomer or lactide, and the finely-powdered filler (D) is inorganic powder.

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7. The porous film of any one of the preceding claims wherein the finely-powdered filler is barium sulfate, calcium carbonate or magnesium oxide.

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8. The porous film of any one of the preceding claims wherein the melting and film-forming is carried out in the temperature range of from 100 to 270°C.

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9. The porous film of any one of the preceding claims wherein the stretching is carried out in the range of from the glass transition temperature of the lactic acid-base polymer to said glass transition temperature + 50°C.

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10. A process for producing a porous film of any one of the preceding claims by the process comprising adding from 40 to 250 parts by weight of a finely-powdered filler having an average particle size of from 0.3 to 4 μ m to 100 parts by weight of a polylactic acid-base resin composition comprising from 80 to 100 % by weight of polylactic acid or a lactic acid-hydroxycarboxylic acid copolymer and from 0 to 20 % by weight of a plasticizer, melting and film-forming the resultant mixture, and successively stretching the thus-obtained film 1.1 times or more to at least one direction of the axis.

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(54) **Porous film.**

(57) Disclosed is a breathable, hydrolyzable, porous film which is obtained by the process comprising adding from 40 to 250 parts by weight of a finely-powdered filler having an average particle size of from 0.3 to 4 μ m to 100 parts by weight of a polylactic acid-base resin composition comprising from 80 to 100 % by weight of polylactic acid or a lactic acid-hydroxycarboxylic acid copolymer and from 0 to 20 % by weight of a plasticizer, melting and film-forming the resultant mixture, and successively stretching the thus-obtained film 1.1 times or more to at least one direction of the axis; and which is consequently useful as a material for leakproof films of sanitary materials such as a paper diaper and packaging materials, and does not accumulate as wastes because of hydrolyzability in the natural environment in the case of being abandoned after use.

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EUROPEAN SEARCH REPORT

Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 272 902 (E.I. DU PONT DE NEMOURS AND COMPANY) * claims * * examples *	1	C08J5/18 C08J9/00 //C08L67:04
A	EP-A-0 050 215 (AMERICAN CYANAMID COMPANY) * claims 1-2,8,17,19-21 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C08J C08K C08L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09 DECEMBER 1992	Examiner PERSSON
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>Δ : member of the same patent family, corresponding document</p>			

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